Title: Complexes of copper(II) with 3-(ortho-substituted phenylhydrazo)pentane-2,4-diones: syntheses,properties and catalytic activity for cyclohexane oxidation

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Abstract: Reactions of copper(II) with 3-phenylhydrazopentane-2,4-diones X-2-C6H4-NHN = C{C(= O)CH3}(2) bearing a substituent in the ortho-position [X = OH (H2L1) 1, AsO3H2 (H3L2) 2, Cl (HL3) 3, SO3H (H2L4) 4, COOCH3 (HL5) 5, COOH (H2L6) 6, NO2 (HL7) 7 or H (HL8) 8] lead to a variety of complexes including the monomeric [CuL4(H2O)(2)]center dot H2O 10, [CuL4(H2O)(2)] 11 and [Cu(HL4)(2)(H2O)(4)] 12, the dimeric [Cu-2(H2O)(2)(mu-HL2)(2)] 9 and the polymeric [Cu(mu-L-6)](n)] 13 ones, often bearing two fused six-membered metallacycles. Complexes 10-12 can interconvert, depending on pH and temperature, whereas the Cu(II) reactions with 4 in the presence of cyanoguanidine or imidazole (im) afford the monomeric compound [Cu(H2O)(4){NCNC(NH2)(2)}(2)](HL4)(2)center dot 6H(2)O 14 and the heteroligand polymer [Cu(mu-L-4)(im)](n) 15, respectively. The compounds were characterized by single crystal X-ray diffraction (complexes), electrochemical and thermogravimetric studies, as well as elemental analysis, IR, H-1 and C-13 NMR spectroscopies (diones) and ESI-MS. The effects of the substituents in 1-8 on the HOMO-LUMO gap and the relative stability of the model compounds [Cu(OH)(L-8)(H2O)]center dot H2O, [Cu(L-1)(H2O)(2)]center dot H2O and [Cu(L-4)(H2O)(2)]center dot H2O are discussed on the basis of DFT calculations that show the stabilization follows the order: two fused 6-membered > two fused 6-membered/5-membered > one 6-membered metallacycles. Complexes 9, 10, 12 and 13 act as catalyst precursors for the peroxidative oxidation (with H2O2) of cyclohexane to cyclohexanol and cyclohexanone, in MeCN/H2O (total yields of ca. 20% with TONs up to 566), under mild conditions.

KeyWords Plus: Mild Peroxidative oxidation; O-2-H2O2-Vanadium Derivative-Pyrazine-2-Carboxylic Acid; Hydrogen-Peroxide; Crystal-Structures; Beta-Diketones; Triethanolamine Complexes; Potential Antineoplastics; Hydrocarbon Oxygenations; Azo Derivatives, Alkanes

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